reaction temperature rose to over 200° in less than 20 minutes and a 68% yield of the *beta*-adduct was isolated.

The use of the copper(I) chloride, the diamine, and the monoamine thus exerts a very powerful catalytic effect on silicon hydride-olefin addition reactions. Inasmuch as the two amines and the acrylonitrile (or other olefin) can each form complexes with copper(I) chloride and possibly with the chlorosilane, it is presently difficult to speculate about a mechanism for this addition reaction. The catalyst system presumably functions as a strong base to polarize the silicon–hydrogen bond, thereby facilitating a *beta*-addition of the silicon to the acrylonitrile. It is also possible that an amine–copper(I)–acrylonitrile complex is formed rendering the olefin double bond more susceptible to nucleophilic attack. Additional experiments pertaining to this catalyst system and addition reaction will be reported later.

SILICONE PRODUCTS DEPARTMENT
GENERAL ELECTRIC COMPANY   BEN A. BLUESTEIN
WATERFORD, NEW YORK

THE REACTION OF MIXED TRIALKYLBORANES WITH ALKALINE SILVER NITRATE—HYDROBORATION AS A CONVENIENT ROUTE FOR THE SYNTHESIS OF CARBON STRUCTURES

Sir:

The very ready coupling of hydroborated olefins *in situ* by silver nitrate in the presence of alkali[1] prompted a study of the reaction of mixed organoboranes with the reagent. The results demonstrate that this new approach to the formation of carbon-to-carbon bonds should possess general applicability for the synthesis of hydrocarbon structures.

Equimolar mixtures of 1-hexene with 1-pentene, 2-methyl-1-butene, cyclopentene and 2-methyl-2-butene were hydroborated and treated in methanolic solution with silver nitrate and potassium hydroxide as described previously.[1] In the case of 1-pentene and 2-methyl-1-butene, the yields of the three possible products were almost statistical: C-10/C-11/C-12 = 1.0/2.0/1.0. In the case of the olefins yielding secondary organoboranes, the yields of the C-11 products drop below those predicted on a statistical basis (Table I).

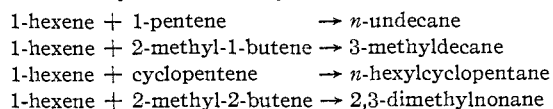TABLE I

EFFECT OF STRUCTURE ON MIXED COUPLINGS WITH 1-HEXENE

Olefin	Ratio 1-hexene/ olefin	Yield,[a] %	Products C-10	C-11	C-12
1-Pentene	1/1	66	1.00	2.00	1.00
2-Methyl-1-butene	1/1	64	0.97	1.88	1.00
Cyclopentene	1/1	54	0.44	1.05	1.00
2-Methyl-2-butene	1/1	52	0.45	1.02	1.00
1-Pentene	3/1	63	1.00	6.00	9.00
2-Methyl-1-butene	3/1	62	1.02	5.35	9.00
Cyclopentene	3/1	58	0.65	4.00	9.00
2-Methyl-2-butene	3/1	59	0.66	3.20	9.00

[a] Combined yield of C-10, C-11 and C-12 products based on the vapor phase chromatographic analysis.

(1) H. C. Borwn and C. H Snyder, *J. Am. Chem. Soc.*, **83**, 1002 (1961).

In a reaction involving a statistical coupling of two different alkyl groups, R and R', the maximum yield of the desired product can only be 50% of the coupled material, R_2, R–R', R'_2. However, there is the possibility of utilizing a large excess of a relatively cheap olefin to achieve a more nearly complete conversion of a second, more expensive olefin into the desired product. The practicality of this approach is indicated in Table I where a three-fold excess of 1-hexene over the C-5 olefin has given much higher conversions of the latter into the desired products.

The power of this new synthetic procedure is indicated by the above syntheses:

1-hexene + 1-pentene → *n*-undecane
1-hexene + 2-methyl-1-butene → 3-methyldecane
1-hexene + cyclopentene → *n*-hexylcyclopentane
1-hexene + 2-methyl-2-butene → 2,3-dimethylnonane

One limitation is evident. The two olefins should preferably differ in molecular weights so that the mixed product, RR', can be separated readily from the symmetrically coupled products, RR and R'R'. Fortunately, this is not a serious limitation since it is usually possible to select reactants to facilitate this separation.[2]

The hydroboration reaction can tolerate many functional groups (*e.g.*, carbethoxy, nitro, sulfone) which cannot be present in Grignard reactions. Consequently, it is evident that this synthetic procedure for achieving desired carbon structures should prove a valuable adjunct to the Grignard synthesis.

(2) For example, the synthesis of 2-, 3-, and 4-methylnonane can be carried out with the appropriate butenes and hexenes, all commercially available.

RICHARD B. WETHERILL LAB.   HERBERT C. BROWN
PURDUE UNIVERSITY   CALVIN VERBRUGGE
LAFAYETTE, INDIANA   CARL H. SNYDER

THE REACTION OF TRIETHYLBORANE WITH OXIDES OF SILVER, GOLD AND PLATINUM—A NEW CONVENIENT ROUTE TO NOBLE METAL ALKYLS AND TO FREE RADICAL CHEMISTRY

Sir:

In recent years the low temperature reaction of silver nitrate with lead alkyls, $R_4Pb + AgNO_3 \rightarrow RAg + R_3PbNO_3$, has been utilized as a convenient route to the unstable silver alkyls and related organometallics.[1] In the course of our program on the chemistry of trialkylboranes, we were led to explore the possible utility of triethylborane for the synthesis of ethylsilver and related noble metal alkyls.[2] The interesting chemical possibilities of these unstable derivatives have long been evident.[3]

(1) C. E. H. Bawn and R. Johnson, *J. Chem. Soc.*, 3923 (1960); C. E. H. Bawn and F. J. Whitby, *ibid.*, 3926 (1960).

(2) The reaction of mercuric oxide and lead (II) oxide with triethylborane at 70–80° has been utilized recently for the synthesis of stable organometallics, such as diethylmercury and tetraethyllead: J. B. Honeycutt, Jr., and J. M. Riddle, *J. Am. Chem. Soc.*, **82**, 3051 (1960).

(3) J. H. Gardner and P. Borgstrom, *ibid.*, **51**, 3375 (1929).

Treatment of 1.00 mmole of triethylborane at 25° with 3.00 mmoles of silver nitrate or 1.50 mmoles of silver oxide in water (2.0 ml.) solution or suspension resulted in only a sluggish reaction, producing only minor amounts of n-butane, ethane and ethylene (decomposition products of ethyl-silver[1]) in 18–24 hours. Thus, in 18 hours the reaction involving silver oxide produced 9% n-butane, 5% ethylene and 15% ethane.

The addition of sodium hydroxide exerted a remarkable effect on the reaction. Thus the presence of 3.0 mmoles of sodium hydroxide in the silver oxide–triethylborane reaction mixture at either 25° or 0° brought about a very rapid reaction, complete in a matter of minutes.

These experiments with the volatile, inflammable triethylborane were carried out in an all-glass high vacuum apparatus. In a typical experiment, triethylborane, 1.00 mmole, was condensed on a mixture of 3.0 mmoles of sodium hydroxide and 1.51 mmole of silver oxide in 2.0 ml. of water. The vessel was warmed to 25° and the pressure observed. Within 10 minutes the pressure rose to 400 mm. and became sensibly constant. The volatile products were removed, measured, and analyzed on a silver nitrate–benzyl cyanide column. There was obtained 1.08 mmoles of n-butane (72%), 0.27 mmole of ethylene (9%), and 0.27 mmole of ethane (9%), accounting for 90% of the ethyl groups.

The reaction proceeds in methanol with similar results. In this solvent it was possible to attempt the reaction at lower temperatures. At −24° the decomposition of the intermediate ethylsilver is slow[1] and the hydrocarbon products appear at a significant rate only if the temperature is raised to 0° and above. No significant difference was observed in experiments in which silver oxide (or hydroxide) was formed *in situ* from silver nitrate and sodium hydroxide.

From these results, it is evident that in contrast to the behavior of tetraethyllead in its reaction with silver nitrate[1] all three ethyl groups of the triethylborane are utilized, Et₃B + 3AgOH + NaOH → 3EtAg + NaB(OH)₄. Consequently, this reaction provides a more economical means of utilizing alkyl groups and permits the preparation of ethylsilver in a medium free of another organometallic as by-product.

In the same way sodium hydroxide brings about a rapid reaction at 25° of triethylborane with auric oxide (formed *in situ* from auric chloride and sodium hydroxide) producing 74% n-butane, 16% ethylene and 1% ethane.[4] The reaction with platinic oxide (formed *in situ* from platinic chloride) was more sluggish and differed also from the preceding reactions in not producing n-butane—the product was predominantly ethane: 57% ethane, 8% ethylene. Triethylborane is quite stable under these conditions in the absence of the platinic oxide.

The decomposition of ethylsilver is believed to involve free radicals.[1] Treatment of silver oxide with sodium hydroxide and triethylborane in the presence of carbon tetrachloride resulted in a

marked decrease in yield of n-butane (12%), with the formation of a considerable amount of ethyl chloride (36%). Similarly, when the triethylborane–silver oxide–sodium hydroxide reaction was carried out in methanol containing styrene (1 M), the production of n-butane was markedly reduced (from 61% to 12%), and styrene largely disappeared from the solution.

These observations suggest that this reaction provides a new, simple route to ethylsilver and related derivatives, as well as a highly promising means of generating free radicals in aqueous and methanolic solutions. We are presently exploring the full scope of this new entry into free radical chemistry.

The financial assistance of the Ethyl Corporation in this study is gratefully acknowledged.

RICHARD B. WETHERILL LAB.   HERBERT C. BROWN
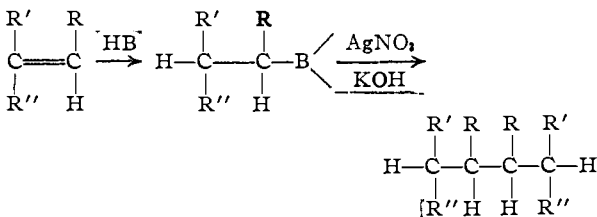PURDUE UNIVERSITY   NORMAND C. HÉBERT
LAFAYETTE, INDIANA   CARL H. SNYDER

THE REACTION OF TRIALKYLBORANES WITH ALKALINE SILVER NITRATE—A NEW GENERAL COUPLING REACTION

Sir:

We wish to report a new general coupling reaction which provides a highly convenient route for the conversion of olefinic derivatives into their saturated dimers. The synthesis involves the hydroboration of the olefinic derivative,[1] followed by the successive treatment *in situ* with solutions of sodium or potassium hydroxide and silver nitrate.[2]

$$\begin{array}{ccc}
\text{R}' \;\; \text{R} & & \text{R}' \;\; \text{R} \\
| \;\;\;\; | & \text{HB} & | \;\;\;\; | \\
\text{C}{=\!=}\text{C} & \longrightarrow & \text{H}-\text{C}-\!-\!-\text{C}-\text{B} \\
| \;\;\;\; | & & | \;\;\;\; | \\
\text{R}'' \;\; \text{H} & & \text{R}'' \;\; \text{H}
\end{array}
\quad
\begin{array}{c}
\nearrow \text{AgNO}_3 \\
\searrow \text{KOH}
\end{array}$$

$$\begin{array}{cccc}
\text{R}' & \text{R} & \text{R} & \text{R}' \\
| & | & | & | \\
\text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\
| & | & | & | \\
\text{R}'' & \text{H} & \text{H} & \text{R}''
\end{array}$$

The coupling reaction for simple terminal olefins, such as 1-butene, 1-hexene and 1-octene, is conveniently carried out with aqueous solutions of the reagents. In this way there was obtained from 1-hexene, coupled at −20°, a 79% yield of dodecane;[3] at 0°, a 71% yield.

1-Hexene, 8.4 g., 0.100 mole, was hydroborated with sodium borohydride and boron trifluoride etherate in 57.5 cc. of diglyme. Water, 20 cc., was added to destroy residual hydride, then 120 cc. of 2.0 M aqueous potassium hydroxide. The mixture

(1) H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957); H. C. Brown, K. J. Murray, L. J. Murray, J. A. Snover and G. Zweifel, *J. Am. Chem. Soc.*, **82**, 4233 (1960).

(2) The reaction of Grignard reagents with silver bromide has been utilized for couplings: J. H. Gardner and P. Borgstrom, *ibid.*, **51**, 3375 (1929). It has also been reported that alkylboronic acids react with ammoniacal silver oxide (Tollens reagent) at elevated temperatures to yield coupled products: H. R. Snyder, J. A. Kuck and J. R. Johnson, *ibid.*, **60**, 105 (1938); J. R. Johnson, M. G. VanCampen, Jr., and O. Grummitt, *ibid.*, **60**, 111 (1938). In the present study ammoniacal silver oxide proved to be unsatisfactory for bringing about the coupling reaction with the trialkylboranes.

(3) The product was predominantly n-dodecane with approximately 6% of 5-methylundecane. The latter presumably arises from the 6% of the secondary boron derivative formed in the usual hydroboration of a terminal olefin: H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **82**, 4708 (1960).

(4) Dimethyliodogold, (CH₃)₂AuI, is stable in ethyl alcohol at room temperature, but is decomposed in this solvent by alkali with the deposition of gold: F. H. Brain and C. S. Gibson, *J. Chem. Soc.*, 762 (1939).